

32692
Customer Number



Patent
Case No.: 56081US002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor: NELSON, JAMES M.

Application No.: 09/824330 Group Art Unit: 1743

Filed: April 2, 2001 Examiner: Handy, Dwayne K.

Title: A CONTINUOUS PROCESS FOR THE PRODUCTION OF
COMBINATORIAL LIBRARIES OF MATERIALS

DECLARATION UNDER 37 C.F.R. 1.131 TO OVERCOME CITED REFERENCE

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

CERTIFICATE OF MAILING	
I hereby certify that this correspondence is being deposited with the United States Postal Service as First Class Mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on:	
May 18, 2005	
Date	Signed by: Judy Knutson

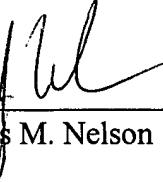
Dear Sir:

This Declaration is being submitted to establish completion of the invention of the above-identified application in the United States on a date prior to March 7, 2001, which is the earliest effective filing date of US 2002/0170976 (Bergh et al.), which has been cited by the Examiner in rejecting the pending claims of the present application.

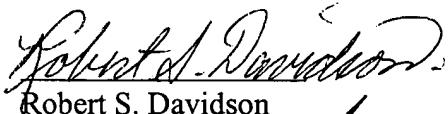
We, James M. Nelson, Robert S. Davidson, Jeffrey J. Cernohous, Michael J. Annen, James R. McNerney, Robert W. Ferguson, Anthony R. Maistrovich, and James A. Higgins, hereby declare that:

1. We are the Applicants of the above-identified patent application and coinventors of the subject matter described and claimed therein.
2. Prior to March 7, 2001, we completed the invention as described and claimed in the above-identified application in this country, the United States of America, as evidenced by a 3M Record of Invention No. N001740, entitled "The Use of Stirred Tubular Reactor Technology (STR) for the Combinatorial Synthesis of Controlled Architecture Materials", a copy of which is attached hereto and marked as Exhibit A. Portions of this Record of Invention have been redacted to protect the confidentiality of the information.

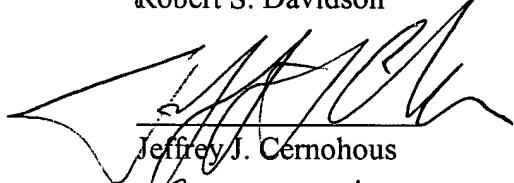
3. From 3M Record of Invention No. N001740, it can be seen that:
 - a. the use and advantages of stirred tubular reactor technology (STR), which is a type of plug-flow reactor technology, is generally described on pages 3-4;
 - b. the introduction of monomer components into an STR-type reactor is generally described, for example, on page 4;
 - c. the changing of variables affecting the components of the reactor in order to produce a combinatorial library of materials is generally described, for example, on page 4-5; and
 - d. experimental examples demonstrating the reduction to practice of the invention are shown on pages 6-21; specifically, in examples 1 and 2 it can be seen that different components were fed into different zones of a plug-flow type reactor, with the feed streams being changed to produce different materials.
4. From page 21 of 3M Record of Invention No. N001740, it can be seen that the invention in this application was made at least by the date of October 1, 1999, which is a date earlier than the effective date of Bergh et al.
5. As a person signing below, I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United states Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.



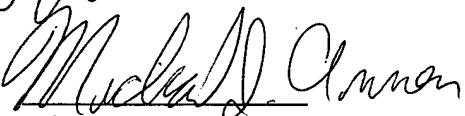
James M. Nelson

Date: 3/21/05

Robert S. Davidson

Date: 3/21/05

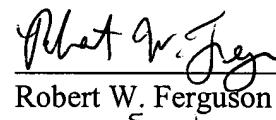
Jeffrey J. Cernohous

Date: 3/21/05

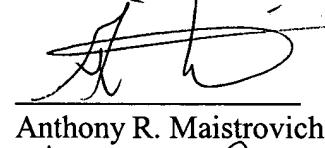
Michael J. Annen

Date: 3/18/05

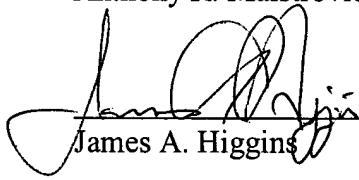
James R. McNerney

Date: 05/03/05

Robert W. Ferguson

Date: 3/21/05

Anthony R. Maistrovich

Date: 3-16-05

James A. Higgins

Date: 3-17-05

Exhibit A



Record of Invention

N001740

Redacted

**The Use of Stirred Tubular Reactor Technology (STR) for the
Combinatorial Synthesis of Controlled Architecture Materials**

Redacted

Description of the Invention

The invention is an economical process for the combinatorial synthesis of controlled architecture materials via the use of stirred tubular reactor technology (STR). The STR is proving to be a powerful tool for the synthesis of these structured materials, such as block copolymeric, end-functionalized and hyperbranched/dendritic polymers, that are not readily available commercially. With the STR it is easy to change conditions on the fly to produce Kg quantities of a variety of Block copolymer compositions on a given day. This would allow researchers access to test kg samples in various applications as a screening mechanism. This would allow us to categorize the materials along certain preset screening criteria and hopefully allow us to build libraries of information that not only includes physical characterization but also an application slant. The invention can be seen as an intermediate step between parallel synthesis and large scale production, where a short list of candidate materials which were identified from large arrays of milligram-level experiments can be scaled continuously and economically to a quantity suitable for screening in product development in a quasi-combinatorial fashion.

Redacted

Utility of Invention

Background

Redacted

Advances in reactor technology have empowered chemists and engineers to rapidly produce large libraries of discrete organic molecules in the pursuit of new drug discovery leading to the development of a blossoming branch of research called Combinatorial Chemistry. Robotic driven parallel synthesizers (Chemspeed, FlexChem(R), Reacto-Stations(TM)) have been designed for such efforts consisting of arrays of small batch type reactors. These reactors synthesize milligram - gram quantities of materials which can rapidly be screened or analyzed by various techniques including gas chromatography, FT-IR, and UV-Visible spectroscopy.

The use of a combinatorial approach for materials synthesis is a relatively new area of research aimed at using rapid synthesis and screening methods to build libraries of polymeric materials and screen catalysts for the synthesis of macromolecules. The current focus of this material-based research is the synthesis of controlled architecture materials: block, graft, dendritic and functionalized polymers.

Redacted

The parallel synthesizers developed for drug synthesis are ideal for the small scale synthesis of materials and catalyst screening. However, new materials evaluation in application development situations of industrial settings typically involves larger quantities of materials (kilograms) than are produced in these small reactor arrays.

Batch reactors also suffer from poor heat transfer characteristics which may have a detrimental effect on the materials produced in batch arrays. Gelation and increased polydispersity due to termination or other side reactions are examples of detrimental effects that can occur in "living" anionic polymerizations, as an example. There exists a need for an economical reactor system that can rapidly produce many formulations in qualities appropriate for application development and bridge the gap between parallel synthesizers and large batch production kettles.

Currently, our research effort aimed at the development of scalable, economical and continuous processes for the production of controlled architecture materials is centered on the use of stirred tubular reactor technology (STR) and "living" anionic polymerizations. The STR is proving to be a powerful synthetic tool for the industrial scale synthesis of well-defined architecturally controlled materials which are thought to be of use in applications such as smart tapes, high temperature pressure sensitive adhesives, electronic grade adhesives, rheological modifiers, dispersants, surfactants, encapsulants for controlled drug delivery and as compatibilizers for blends applications. In general anionic polymerizations require:

1. Air and water free environments
2. Rigorously pure, inhibitor-free monomers, dry deoxygenated solvents and initiator.
3. Accurate determination of initiator and monomer concentrations
4. Precise temperature, pressure and mixing control, particularly in the case of anionic polymerizations which can be very exothermic.

Anionic polymerizations can be carried out in batchwise fashion. However, batch processes suffer the

following disadvantages:

- a) The exothermic nature of anionic polymerizations requires a reactor with exceptional heat transfer characteristics. The low surface to volume ratio of batch reactors precludes high solid content polymerizations from being examined. It is possible to reach high solids loading by repetitive charging of smaller aliquots. This procedure however introduces additional points where impurities and moisture may be added which result in termination of some of the growing polymer chains and an increase in polydispersity which may detrimentally effect performance of these block copolymers.
- b) In terms of product throughput, batch synthesis techniques do not afford high levels of throughput.
- c) Batch reactors would have to be cleaned between runs and rigorously dried to enable future anionic polymerizations. This increases the chance of reactor contamination and decreases productivity.

The stirred tubular reactors has many advantages over these other processes. The plug-flow nature of the STR provides the ability to synthesize materials in a continuous fashion.

- a) The design of the reactor provides a high surface to reactor volume which facilitates excellent heat transfer. This enables continuous reactions which may be highly exothermic, such as anionic polymerizations, to be carried out with great ease, even at high solid loadings.
- b) The multiple feed ports and ability to feed reactant streams into the reactor at a variety of locations is ideal for the synthesis of block copolymer, end functional or starbranched structures.
- c) The STR also offers intimate and efficient mixing which is vital to the production of homogeneous materials, particularly at high solids levels.
- d) The continuous nature of the reaction does not require high levels of raw materials to be in use at any one period in time, unlike large scale batch reactions. This is a major advantage of the STR due to the toxic nature of typical monomers used in anionic polymerizations (dienes, styrenics, vinyl pyridine, methacrylates).

- e) Isolation and recovery of the reaction solvents is much more manageable in the case of the STR due to the lower quantities in use. These materials can be recycled into the polymerization process after devolitilization in the List..
- f) Continuous STR-based polymerizations may show less product compositional variability over time. This is due to the fact that once the STR process is initiated, there are no additional cleaning or drying procedures as is the case with batch processes. Once clean and dry the reactor stays clean and dry.

Continuous Combinatorial Synthesis of Controlled Architecture Polymers

The ability to control feed flows, locations and compositional variances in the STR provides an opportunity to produce kilogram quantities of a variety of polymer compositions in a continuous, economical, and scaleable fashion.

1) The Process (Figure 1)

The feed streams of monomers (eg. isoprene, styrene, vinyl pyridine, and t-butyl, isodecyl, and glycidyl methacrylate) and solvents (toluene, cyclohexane, tetrahydrofuran) are pressure fed into the STR reactor through purification columns containing alumina (for monomer inhibitor removal) or molecular sieves (water removal) and the sec-butyl lithium initiator is pumped as a slurry in cyclohexane. Flow rates for these feeds are carefully monitored by flow meters as a means of controlling molecular weight and percent solids content. The high surface area to reactor volume ratio in the STR allows for highly exothermic or high solids-loading reactions to be carried out with great ease. For the synthesis of poly(isoprene-4-vinyl pyridine). Polymerizations with isoprene (or Styrene) solids content of 35-45 % are carried out with un-optimized residence times of less than ca.22 minutes through the first three of five independant temperature control zones, followed by addition of the vinyl pyridine at the start of the fourth zone. The last zone is used to add an alcohol quenching agent (isopropanol, methanol etc) and the viscous solution is fed into product pails for vacuum drying or the List devolitilizer. The polymer solution can be devolitilized under vacuum (4-20 torr) at 150 C and melt extruded as a solvent and monomer-free material.

2) A combinatorial approach to materials synthesis with the STR involves varying various components of the block copolymer without termination of the initial polymerization run:

i) Variation of Block Size

The "living polyisoprene" moiety travels through the STR in a plug flow fashion and upon the addition of vinyl pyridine in zone four, a block copolymer is formed with a PI:VP ratio predetermined by the monomer (isoprene, vinyl pyridine) flow rate. The molecular weight of the vinyl pyridine block is readily modified by changes in the vinyl pyridine monomer flow rate without any need to terminate the polyisoprene reaction. Additionally, changes in the isoprene portion of the block copolymer can be effected by variations in isoprene flow rates followed by addition of the appropriate second monomer.

ii) Variation of Molecular Weight.

The overall molecular weight of the block copolymers can be modified by changing the isoprene and vinyl pyridine flow rates while holding the ratio of corresponding block sizes constant. This is accomplished by modifying the initiator flow rate.

iii) Variation of Architecture

Polymer architecture can be changed by variation of catalyst or quenching agents. The use of a difunctional initiator or multiarmed quenching agent can be used to produce starbranched or triblock copolymers while holding monomers flows constant and simply changing initiator/quenching sources. Additionally, difunctional monomers such as divinylbenzene or chloromethylstyrene can be added to existing streams in small increments to produce hyperbranched materials.

iv) Applicable Material Classes

In addition to the poly(isoprene-vinyl pyridine) and poly(styrene-methacrylate) examples provided here, this approach is applicable to other anionically polymerizable monomers such as styrenics (Styrene and it's derivatives), methacrylates, dienes and siloxanes. In addition to block copolymers the STR can be used to produce end-functionalized, starbranched, dendritic, and hyperbranched homo- or block copolymer derivatives of the aforementioned monomer classes in a combinatorial fashion.

v) Other Polymerization Mechanisms

The STR is well situated for combinatorial polymer synthesis employing other living chemistries such as

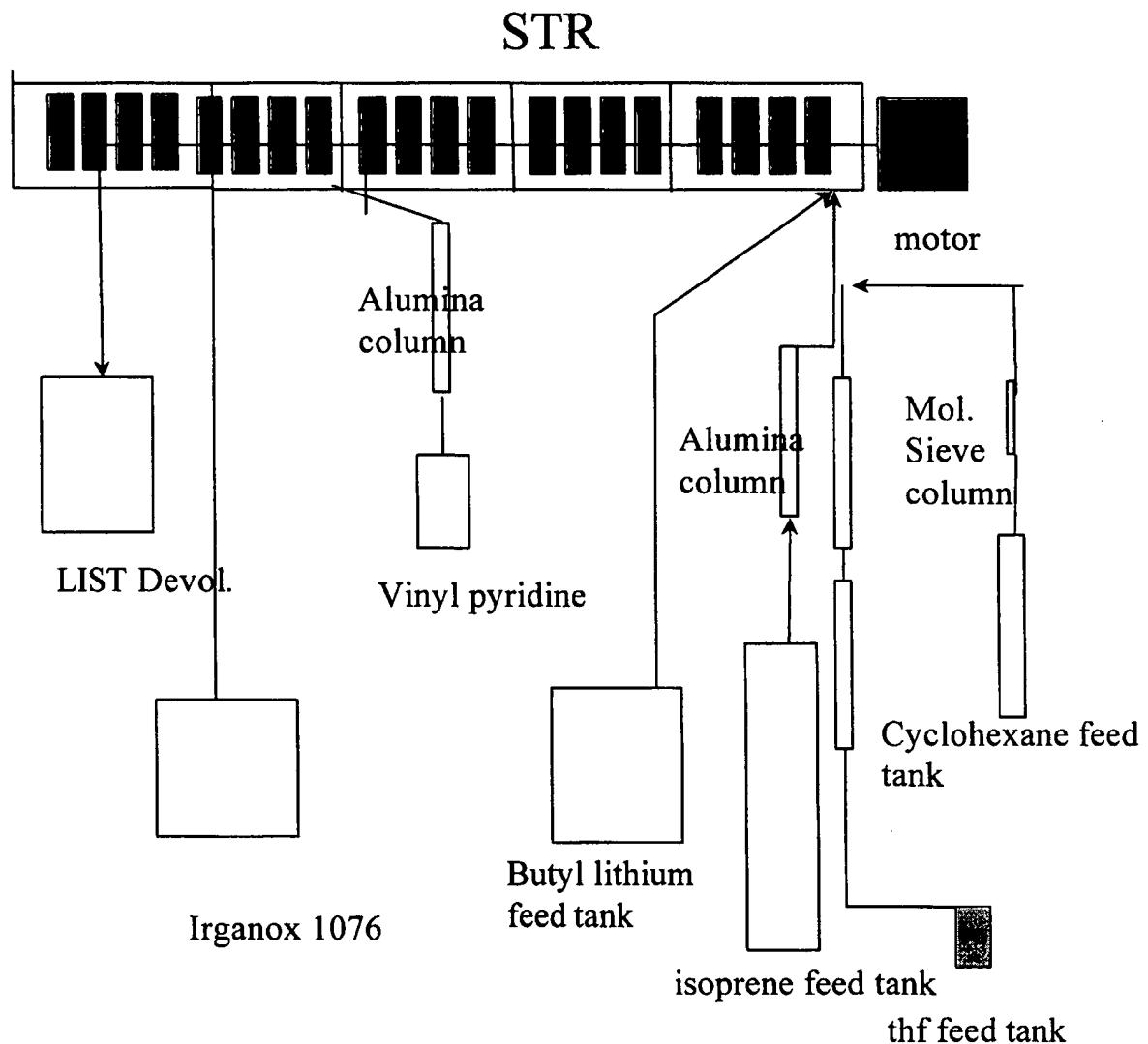
- a) Atom Transfer Radical Polymerizations (ATRP),
- b) the nitroxide-mediated (Tempo) polymerization of acrylates and styrene,
- c) Reversible Addition - Fragmentation transfer RAFT,
- d) cationic polymerizations of THF, α -methylstyrene

Redacted

Figure 1.

Redacted

10 L STR Anionic Polymerization Process



Examples

Example 1. Variation of Block Size

A series of poly(isoprene-vinyl pyridine) (PI-VP) block copolymers of varying molecular weight and respective block sizes were made in the STR (refer to Figure 1). An initial attempt was made to

increase the size of the vinyl pyridine block of the copolymer by varying the vinyl pyridine flow rate (see flow sheet 1-4). The resultant block copolymer would be purged from the reactor over time and vinyl pyridine flows rates suspended for a short time span to provide a short gap between different 'plugs' of materials. After an adjustment of the vinyl pyridine flow rate, addition of the comonomer is resumed to form a new plug of material that is of a new composition. *Note: also in some cases the butyl lithium and isoprene flow rates were altered to adjust % solids and account for the increased solution viscosity encountered with higher VP content polymers.* The materials plugs are separated by samples of polyisoprene due to it's different colour and solution viscosity is readily identified and collected separately, avoiding cross-contamination of the samples. The plug flow characteristics of the reactor facilitate the ease of separation of these fractions. This procedure is continued to make different vinyl pyridine block sizes, while holding the isoprene content constant. The overall molecular weight of each block can be altered easily by changing both flow rates for the monomers.

Cyclohexane/THF (95:5) and the sec-butyl lithium initiator are fed separately into zone one of the reactor at the set flow rates. THF is present in the system to increase the rate of isoprene polymerization. Inhibitor and water are removed from the isoprene and cyclohexane by passing these feed streams through basic alumina and molecular sieves respectively. The temperature of each of the 5 reaction zones is controlled individually by variation of coolant temperatures in the cooling jackets for each zone. Upon initiation, a yellow colored reaction mixture is observed in the first zone. The presence of the THF in this polymerization results in a vigorous exotherm, which with cooling from the jackets is maintained just below the boiling point of the solvents (ca. 60 - 63 C). The materials flow through the first 3 zones in a plug-like fashion, facilitated by the pressure feeding of monomers and stirring paddles along the reaction path, to form "living" polyisoprene materials. At zone #4, vinyl pyridine is added as a solution in cyclohexane (after inhibitor removal with alumina) and a block copolymer is formed. The last zone is used to add an alcohol quenching agent (isopropanol, methanol etc) and the viscous solution is fed into product pails for vacuum drying or the List devolitilizer. The polymer solution can be devolitized under vacuum (4-20 torr) at 150 C and melt extruded as a golden yellow material. Various poly(isoprene-vinyl pyridine) block copolymer materials were synthesized over the span of a few hours each in multi-kilogram quantities, by subtle variations of flow rates. :

a) PI-VP Mw = 30,000 PI/ 3,000 VP - Flow Sheet 1

CombiBlock w. 4-vinylpyridine 3000	30000/3000	
Total solids		26.2079
% Isoprene	20	
% Cyclohexane	60	
Molar ratio of pvinylpyridine to isoprene	0.06515884	
Run Conditions:		
Date	6/17/99	
Temperature	(C)	30
Residence Time(through first 4 zones)	min	22.50
[Isoprene]	mol/L	1.77
[I] in Zone 1	mol/L	4.02E-03
[Isoprene]/[I]		440.40
Predicted Mol. Wt pisoprene	g/mol	30000.00
[4-vinylpyridine] added after zone 3	mol/L	1.14E-01
[I] in Zone 3	mol/L	3.99E-03
[4-vinylpyridene]/[I]		28.56
Predicted Mol. Wt polyvinylpyridine	g/mol	3002.72
Flowrates:		
Cyclohexane	g/min	88.83
isoprene	g/min	32.13
butyl lithium	ml/min	9.72
4-vinylpyridine	g/min	3.23
Irganox 1076	g/min	3.17

b) PI-VP Mw = 30,000 PI/ 6,000 VP - Flow Sheet 2

CombiBlock w. 4-vinylpyridineMn = 6,000

Total solids		27.9338
% Isoprene	20	
% Cyclohexane	60	
molar ratio of pvinylpyridine to isoprene	0.13031768	
Run Conditions:		
date	6/17/99	
Temperature	(C)	30
Run Time	min	720
Residence Time(through first 4 zones)	min	22.50
[Isoprene]	mol/L	1.77
[I] in Zone 1	mol/L	4.02E-03
[Isoprene]/[I]		440.40
Predicted Mol. Wt pisoprene	g/mol	30000.00
[4-vinylpyridine] added after zone 3	mol/L	2.25E-01
[I] in Zone 3	mol/L	3.94E-03
[4-vinylpyridene]/[I]		57.12
Predicted Mol. Wt polyvinylpyridine	g/mol	6005.43
Flowrates:		
Cyclohexane	g/min	88.83
isoprene	g/min	32.13
butyl lithium	ml/min	9.72
4-vinylpyridine	g/min	6.46
Irganox 1076	g/min	3.17
product output	kg	27.78
Butyl lithium charge tank		
Cyclohexane	6691.57 ml	5199.35 g
butyl lithium soln.	308.43 ml	213.74 g

c) PI-VP Mw = 30,000 PI/ 9,000 VP - Flow Sheet 3

ComboBlock w. 4-vinylpyridine Mn = 9000

Total solids		32.5434
% Isoprene	25	
% Cyclohexane	65	
molar ratio of pvinylpyridine to isoprene	0.1956755	
Run Conditions:		
date	6/17/99	
Temperature	(C)	30
Run Time	min	720
Residence Time(through first 4 zones)	min	22.50
[Isoprene]	mol/L	2.48
[I] in Zone 1	mol/L	5.63E-03
[Isoprene]/[I]		440.40
Predicted Mol. Wt pisoprene	g/mol	30000.00
[4-vinylpyridine] added after zone 3	mol/L	4.61E-01
[I] in Zone 3	mol/L	5.38E-03
[4-vinylpyridene]/[I]		85.73
Predicted Mol. Wt polyvinylpyridine	g/mol	9013.44
Flowrates:		
Cyclohexane	g/min	107.34
isoprene	g/min	45.02
butyl lithium	ml/min	12.50
4-vinylpyridine	g/min	13.60
Irganox 1076	g/min	4.45
product output	kg	42.20
Butyl lithium charge tank		
Cyclohexane	8567.81 ml	6657.19 g
butyl lithium soln.	432.19 ml	299.51 g

Redacted

d) PI-VP Mw = 42,000 PI/ 7,000 VP- Flow Sheet 4.

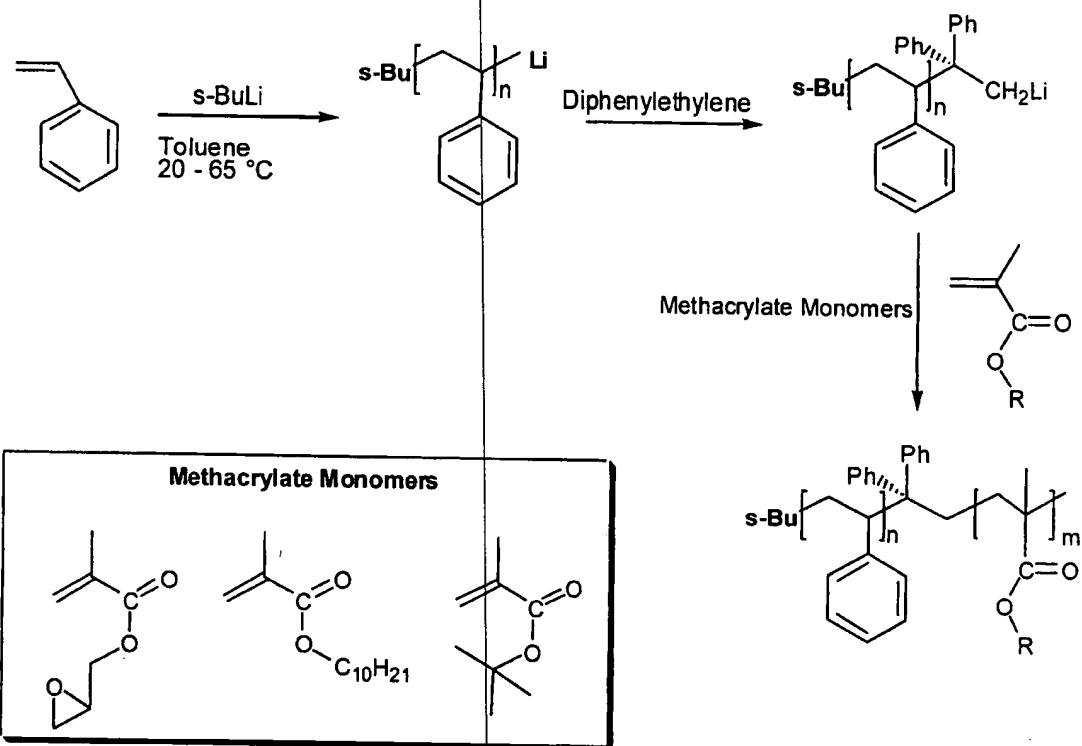
ComboBlock w. 4-vinylpyridine Mn =15,000

Total solids		32.7655
% Isoprene	25	
% Cyclohexane	65	
molar ratio of pvinylpyridine to isoprene	0.19526886	
Run Conditions:		
date	6/17/99	
Temperature	(C)	30
Run Time	min	720
Residence Time(through first 4 zones)	min	22.50
[Isoprene]	mol/L	2.48
[I] in Zone 1	mol/L	4.02E-03
[Isoprene]/[I]		617.12
Predicted Mol. Wt pisoprene	g/mol	42038.10
[4-vinylpyridine] added after zone 3	mol/L	4.60E-01
[I] in Zone 3	mol/L	3.83E-03
[4-vinylpyridene]/[I]		120.06
Predicted Mol. Wt polyvinylpyridine	g/mol	12622.85
Flowrates:		
Cyclohexane	g/min	107.34
isoprene	g/min	45.02
butyl lithium	ml/min	12.50
4-vinylpyridine	g/min	13.57
Irganox 1076	g/min	3.17
product output	kg	42.18
Butyl lithium charge tank		
Cyclohexane	8691.57 ml	6753.35 g
butyl lithium soln.	308.43 ml	213.74 g

Redacted

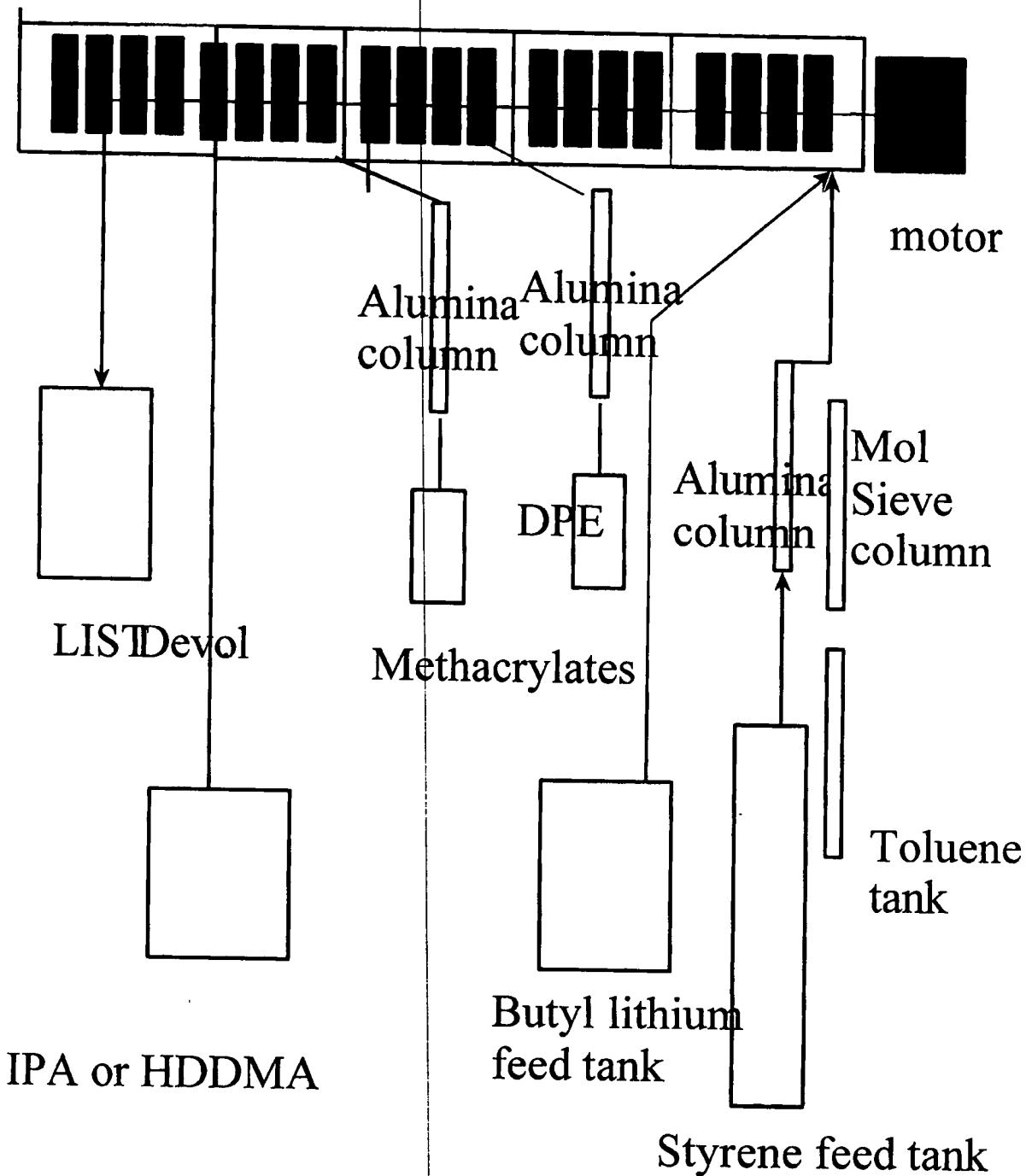
Example 2. Variation of Block Type- Poly(styrene-methacrylate) Block Copolymers

Styrene, toluene and the sec-butyl lithium initiator are separately fed into zone one of the reactor at the set flow rates. Inhibitor and water are removed from the styrene and toluene by passing these feed streams through basic alumina and molecular sieves respectively. The temperature of each of the 5 reaction zones is controlled individually by variation of coolant temperatures in the cooling jackets for each zone. Upon initiation, a red colored reaction mixture is observed in the first zone. A vigorous exotherm results, which with cooling from the jackets is maintained at 60 - 63 C. The solution flows through the first 2 zones in a plug-like fashion, facilitated by the pressure feeding of monomers and stirring paddles along the reaction path, to form "living" polystyrene materials. In Zone 3, diphenylethylene is added, resulting in a burgandy colored solution, to reduce the nucleophilicity of the polystyryl anion and allow for the efficient polymerization of polar monomers (ie. methacrylates). At the start of zone #4, t-butyl methacrylate (tBMA) is added (after inhibitor removal with alumina) resulting in a lime green solution indicative of styrene/methacrylate block copolymer formation (Flow sheet 5). In addition, starbranched PS-methacrylate blocks can be synthesized by addition of hexanediol dimethacrylate (HDDMA) in the fifth reaction zone.



As in Example 1 feed streams can be changed to produce different materials without the need to stop and restart the toluene, styrene, DPE or initiator flows. An example of such a combinatorial approach is outlined as follows. 30 minutes later, the t-BMA and HDDMA flows were terminated and to this living DPE-functionalized PS solution the IDMA flow was initiated. This results in the formation of linear PS-DPE-IDMA block copolymers (Flowsheet 6). Once again the addition of HDDMA to the linear block results in starbranched PS-DPE-IDMA block copolymers. Similar cycling of flows

can be done with additional monomers such as glycidyl methacrylate, forming linear and starbranched PS-DPE-GMA block copolymers (Flowsheet 7). This reaction scheme takes place with no intermixing of the various products due to the plug flow nature of the reactor.



Flow Sheet 5. PS-DPE-t-BMA Mw = 20,000 PS/ 6,000 t-BMA and starbranched

PS-DPE-t-BMA***Styrene Polymerization on 10L STR***

Copolymer w. tbma

Run No.

2

Physical Constants:**Densities**

Styrene	0.909 g/ml
toluene	0.943 g/ml
IPA	0.785 g/ml
Density of Reactor Soln.	0.92974 g/ml
Butyl Lithium(1.3M)	0.769 g/ml
THF	0.985 g/ml
tbma	0.875 g/ml
dpe	1.021 g/ml
Butyl Lithium Conc. in Cyclohexane	1.3

% Irganox 1076 in cyclohexane	10
%Styrene	39
Total Solids	42.5074081

Molecular Weights:

styrene	104.15 g/mol
butyl lithium	64.06 g/mol
tbma	142.5 g/mol
p-TSA	190.22 g/mol
dpe	180.25 g/mol
molar ratio of tbma to pstyrene	0.22676228
wt fraction Dpe in cyclohexane	5

Run Conditions:

Temperature	(C)	30
Run Time	min	480
Residence Time(through first 2 zones)	min	15.00
[Styrene]	mol/L	3.48
[I] in Zone 1	mol/L	1.81E-02
[Styrene]/[I]		192.03
Predicted Mol. Wt Styrene	g/mol	20000.00
[tbma] added after zone 3	mol/L	6.57E-01
[I] in Zone 3	mol/L	1.58E-02
[tbma]/[I]		41.50
Predicted Mol. Wt polytbma	g/mol	5913.23
Conversion	%	100

Redacted

Page 14

Flowrates:

Total flow(Zones 1-2)	ml/min	266.67
Total flow(Zones 1-2)	g/min	247.93
Toluene	ml/min	145.80
Toluene	g/min	137.49
styrene	ml/min	106.37
styrene	g/min	96.69
butyl lithium	ml/min	14.58
butyl lithium	g/min	13.75
dpe added after zone 2	g/min	20.12
dpe added after zone 2	ml/min	19.70
tbma added after zone 3	g/min	30.00

StarBranched**HDDMA**

HDDMA	619.35 g
Toluene	5574.14 g
HDDMA for 1 hr	77.42
Toluene for 1Hr	696.77
HDDMA	g/min
	12.90

**Flow Sheet 6. PS-DPE-IDMA Mw = 20,000 PS/ 9,000 IDMA and starbranched
PS-DPE-IDMA**

Redacted

Page 16

Styrene Polymerization on 10L STR
 Copolymer w. IDMA
 Run No.
Physical Constants:

1

Densities

Styrene	0.909 g/ml	
toluene	0.943 g/ml	
IPA	0.785 g/ml	
Density of Reactor Soln.	0.92974 g/ml	
Butyl Lithium(1.3M)	0.769 g/ml	
THF	0.985 g/ml	
IDMA	0.878 g/ml	
dpe	1.021 g/ml	
Butyl Lithium Conc. in Cyclohexane		1.3
%ipa	10	
%Styrene	39	

Molecular Weights:

styrene	104.15 g/mol	
butyl lithium	64.06 g/mol	
IDMA	226.36 g/mol	
IPA	60.1 g/mol	
dpe	180.25 g/mol	
molar ratio of IDMA to pstyrene	0.21412987	
wt fraction Dpe in cyclohexane	5	

Run Conditions:

Temperature	(C)	30
Run Time	min	480
Residence Time(through first 2 zones)	min	15.00
[Styrene]	mol/L	3.48
[I] in Zone 1	mol/L	1.81E-02
[Styrene]/[I]		192.03
Predicted Mol. Wt Styrene	g/mol	20000.00
[IDMA] added after zone 3	mol/L	5.89E-01
[I] in Zone 3	mol/L	1.50E-02
[IDMA]/[I]		39.18
Predicted Mol. Wt polyIDMA	g/mol	8869.84
IPA	% in polymer	0.26
IPA	mol/L	1.81E-02
Conversion	%	100

Flowrates:

Total flow(Zones 1-2)	ml/min	266.67
Total flow(Zones 1-2)	g/min	247.93
Toluene	ml/min	145.80
Toluene	g/min	137.49
styrene	ml/min	106.37
styrene	g/min	96.69
butyl lithium	14.58
butyl lithium	g/min	13.75

Redacted

Starbranched

HDDMA

HDDMA

Toluene

HDDMA for 1 hr

Toluene for 1Hr

HDDMA

619.35 g	
5574.14 g	
77.42	
696.77	
g/min	12.90

Redacted

Page 18

Flow Sheet 7. PS-DPE-GMA Mw = 20,000 PS/ 1,000 t-BMA and starbranched PS-DPE-GMA

Redacted

Page 19

Styrene Polymerization on 10L STR

Copolymer w.GMA

Run No.

Physical Constants:

1

Densities

Styrene	0.909 g/ml
toluene	0.943 g/ml
IPA	0.785 g/ml
Density of Reactor Soln.	0.92974 g/ml
Butyl Lithium(1.3M)	0.769 g/ml
THF	0.985 g/ml
GMA	1.042 g/ml
dpe	1.021 g/ml
Butyl Lithium Conc. in Cyclohexane	1.3
%ipa	10
%Styrene	39

Molecular Weights:

styrene	104.15 g/mol
butyl lithium	64.06 g/mol
GMA	142.16 g/mol
IPA	60.1 g/mol
dpe	180.25 g/mol
molar ratio of gma to pstyrene	0.03788071
wt fraction Dpe in cyclohexane	5

Run Conditions:

Temperature	(C)	30
Run Time	min	480
Residence Time(through first 2 zones)	min	15.00
[Styrene]	mol/L	3.48
[I] in Zone 1	mol/L	1.81E-02
[Styrene]/[I]		192.03
Predicted Mol. Wt Styrene	g/mol	20000.00
[GMA] added after zone 3	mol/L	1.21E-01
[I] in Zone 3	mol/L	1.74E-02
[GMA]/[I]		6.93
Predicted Mol. Wt polyGMA	g/mol	985.45
IPA	% in polymer	0.26
IPA	mol/L	1.81E-02
Conversion	%	100

Flowrates:

Total flow(Zones 1-2)

Redacted

Page 20

ml/min

266.67

Starbranched

HDDMA

HDDMA

Toluene

HDDMA for 1 hr

Toluene for 1Hr

HDDMA

619.35 g	
5574.14 g	
77.42	
696.77	
g/min	12.90

Signature Information

Described by

James Nelson

Signed on:

September 30, 1999

*This document has been read and understood
by me:*

Barry Heldman

Witnessed on:

October 1, 1999

Redacted

Page 21

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.